

## Research Article

# Evaluation of Nitrilotrimethylene Phosphonic Acid and Nitrilotriacetic Acid as Corrosion Inhibitors of Mild Steel in Sea Water

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The inhibition efficiency of nitrilotrimethylene phosphonic acid (NTP) in controlling mild steel corrosion in sea water has been evaluated by galvanostatic polarization, electron scanning for chemical analysis (ESCA), and scanning electron microscope (SEM) methods. The results are compared with those obtained for nitrilotriacetic acid (NTA). NTP is found to be more effective in protecting mild steel against sea water corrosion as compared to NTA. The surface of mild steel in presence and absence of NTP and NTA is characterized by ESCA and SEM. From the ESCA studies, it is found that NTP formed a stable and compact film over the mild steel.

## 1. Introduction

Sea water is a complex natural electrolyte. The corrosion is severe due to the presence of chloride ions and dissolved oxygen. Sea water has been used as cooling fluid in various industries. So, it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used in sea water. Phosphonic acids are extensively used nowadays due to their complex forming abilities. They are also widely used due to their low toxicity, high stability, and high-scale inhibition properties [1–7]. Mild steel is used extensively for its technological properties. The present study aims to (i) find out the corrosion inhibition effects of phosphonic acid groups on mild steel in sea water medium by using nitrilotrimethylene phosphonic acid (NTP) and compare the results with those for nitrilotriacetic acid (NTA), (ii) study the nature of the film on the mild steel surface by using ESCA and SEM, and (iii) propose a mechanism of the corrosion inhibition for the inhibitors in sea water.

## 2. Experimental

**Specimen.** Mild steel (C = 0.15%, Mn = 1.02%, Si = 0.085, S = 0.025%, and P = 0.025%) of 2 mm thickness was used. The specimen was cut in to 1 cm × 1 cm for galvanostatic studies

and 0.5 cm × 0.5 cm for ESCA and SEM studies. Each mild steel specimen was carefully coated with epoxy resin leaving one cm<sup>2</sup> flat surface uncoated. The exposed surface was polished with emery papers of 150, 320, 400, and 600 grades and finally with 4/0 polishing paper. The surface cleaning was done in ultrasonic cleaner Ralsonic model R-30/40 using deionised water.

For galvanostatic studies, potentials were measured with the help of digital potentiometer against saturated calomel electrode with platinum electrode as counter electrode. The open circuit potential was achieved in 6 hours.

X-ray photoelectron Spectroscope ESCA-750, Shimadzu, was used. It was operated at  $5 \times 10^{-9}$  torr with MgK $\alpha$  X-ray radiation (1253.6 eV). SEM studies were done with JEOL840 SEM operated at 10 KV in the secondary electron mode.

**Chemicals.** Nitrilotriacetic acid (NTA), Sigma-Aldrich, USA, was used. NTP was synthesized from NTA. Natural aerated sea water with salinity of 36.1 ppt was used.

## 3. Results and Discussion

**3.1. Galvanostatic Polarisation.** Figure 1 shows the typical polarization curves for mild steel in sea water in the presence of NTP and NTA. The corrosion current densities ( $I_{corr}$ ),  $E_{corr}$

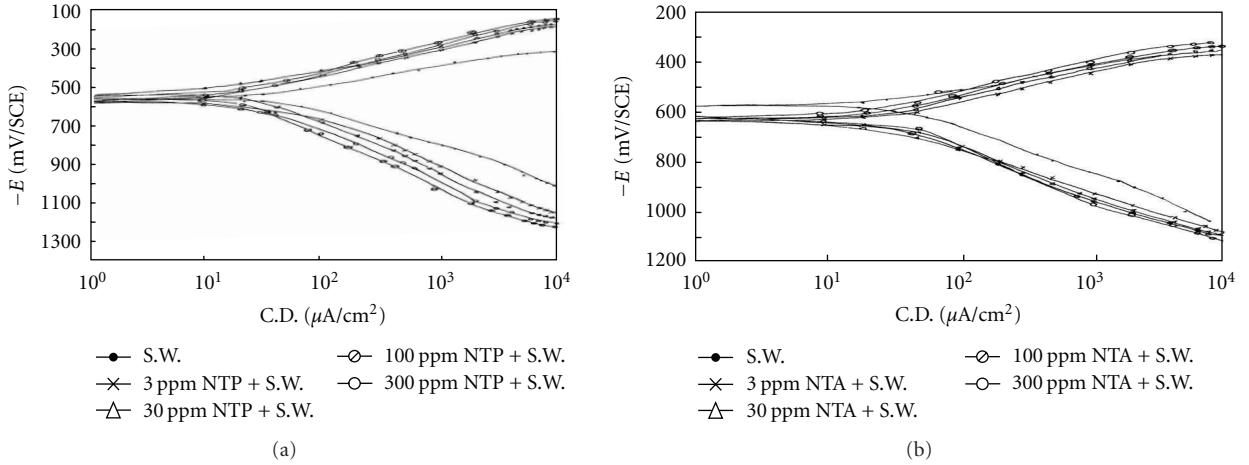


FIGURE 1: Galvanostatic polarization curves for mild steel in sea water in presence of different concentrations of (a) NTP and (b) NTA.

and Tafel slope values are calculated and are given in Table 1. Corrosion current is found to the presence of both NTP and NTA although the effect is more pronounced in the presence of NTP. Therefore, NTP inhibits the corrosion of mild steel in sea water media better than NTA. The lower inhibition efficiency of NTA may be attributed to lesser adsorption and to greater solubility of corrosion products [8]. The inhibition efficiency increases with increase in concentration of NTP till 100 ppm and then decreases. This may be due to dissolution of the oxide outer layer. The inhibitor efficiency of NTA is found to increase with concentration.

The values of Tafel slopes ( $b_c > b_a$ ) in sea water suggest the predominance of oxygen reduction reaction as predicted by Deslouis et al. [9]. The presence of NTP and NTA increases and decreases  $b_c$ , respectively, whereas  $b_a$  almost is unaffected in both the cases.

The presence of NTP does not produce any significant change in the  $E_{\text{corr}}$  value whereas the presence of NTA shifts the  $E_{\text{corr}}$  value in the cathodic direction. Therefore, NTP is a mixed type of inhibitor and suppresses both anodic and cathodic partial processes whereas NTA mainly acts by suppressing the cathodic partial processes.

Marcus and Herbelin [10] have proposed that an exchange takes place between  $\text{Cl}^-$  and  $\text{OH}^-$  ions in the passive layer in chloride environment. Several modes of inhibition in solution containing chloride ions have been suggested [11, 12] including blocking of adsorbed  $\text{Cl}^-$  ions by competitive adsorption. NTP might be inhibiting by formation of  $[\text{Fe-OH-NTP}]_{\text{ad}}$  and  $[\text{Fe-OH-Cl-NTP}]_{\text{ad}}$  film over iron surface.

The inhibition efficiency of NTA is lower than that of NTP molecules. NTA molecules are adsorbed over the metal surface by (i)  $\text{p}\ddot{\text{\i}}\text{-d}\ddot{\text{\i}}$  interaction and (ii) ion pair adsorption between iron and NTA molecules. The adsorbed layers block the penetration of chloride ions onto the metal surface. The lower inhibition efficiency can be attributed to lower adsorption of NTA molecules as compared to NTP molecules. The lower efficiency may also be attributed to greater solubility of corrosion products [8].

**3.2. ESCA Studies.** Binding energies of various elements are reported in Table 2.

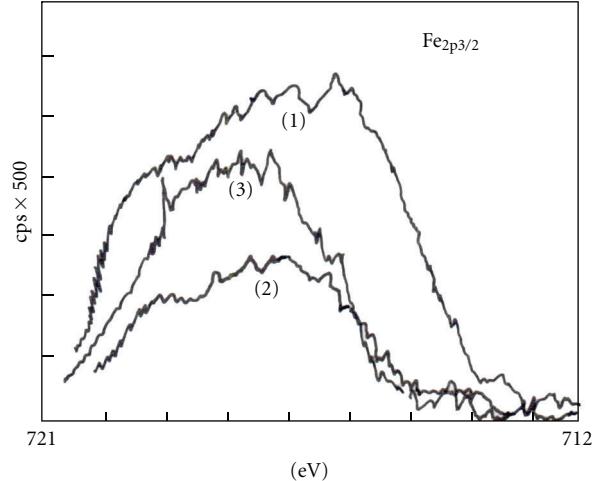


FIGURE 2: XPS spectra of iron ( $\text{Fe}_{2\text{p}3/2}$ ) (1) in sea water, (2) in presence of 300 ppm of NTP, and (3) in presence of 300 ppm of NTA.

More of oxygen and less chloride are present on the surface in case of mild steel sample in sea water. Two peaks of  $\text{O}_{1\text{s}}$  indicate presence of both oxide and hydroxide. The  $\text{Fe}_{2\text{p}3/2}$  peak at 717.3 eV (Table 2) suggests existence of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  in the film [1, 7, 13–16] (Figure 2(1)). The presence of  $\text{Cl}_{2\text{p}3/2}$  at 204.3 eV indicates chloride adsorption over the metal surface (Figure 3(1)). It is clear from the depth profile that the amount of iron increased and that of oxygen decreased during successive etchings.

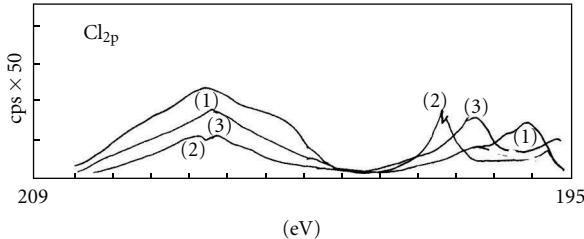
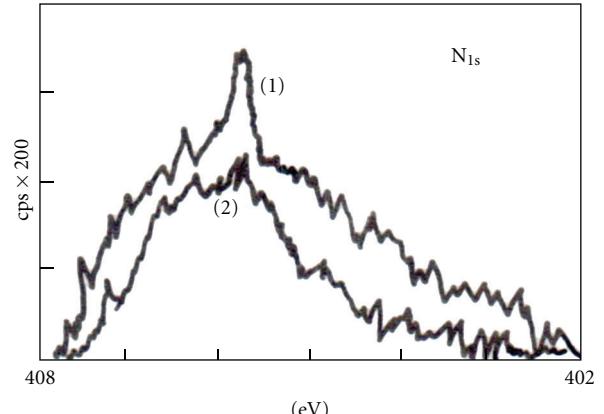
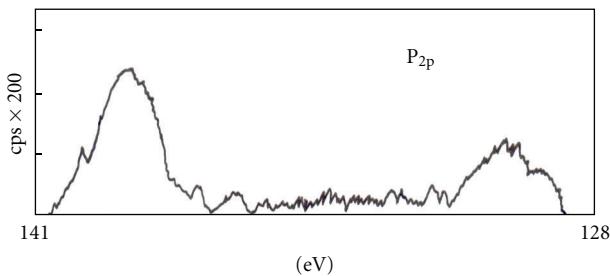
A broad peak at 717.6 eV indicates the presence of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  on the surface of mild steel in 300 ppm of NTP (Figure 2(2)). Two peaks are observed for  $\text{Cl}_{2\text{p}}$  (197.7 eV and 205.4 eV) (Figure 3(2)) and  $\text{P}_{2\text{p}}$  (139.1 eV and 130.6 eV) (Figure 4). One peak is observed for  $\text{C}_{1\text{s}}$  (290.4 eV) and one for  $\text{N}_{1\text{s}}$  (405.7 eV) (Figure 5(1)) in presence of 300 ppm NTP (Table 2). The presence of these elements indicated the film formed to be a thick one [3]. Two peaks of  $\text{O}_{1\text{s}}$  indicate presence of both oxide and hydroxide (Figure 6(a)). This

TABLE 1: Corrosion parameters of mild steel in sea water in presence of inhibitors at 298 K.

Concentration (ppm)	$-E_{corr}$ (mV)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$b_c$ (mV/dec)	$b_a$ (mV/dec)	Inhibition efficiency ( $I\%$ )
0	564	53.0	255	145	—
3 NTP	590	13.5	320	125	74.5
30 NTP	555	11.0	315	125	79.2
100 NTP	550	6.5	310	125	87.7
300 NTP	585	8.0	305	135	84.9
3 NTA	644	32.0	180	115	39.6
30 NTA	638	29.0	180	115	45.3
100 NTA	630	27.0	180	115	49.1
300 NTA	625	25.5	180	125	51.9

TABLE 2: Binding energies (eV) of elements present on mild steel surface after and before treatment with inhibitors.

Solution	Fe 2p <sub>3/2</sub>	O 1S O	O 1S OH	Cl 2p <sub>1/2</sub>	Cl 2p <sub>3/2</sub>	P 2p	C 1S	N 1S
Sea water	717.3	—	537.5	—	204.3	—	—	—
3 ppm NTP	718.2	536.7	537.6	197.6	203.7	140.0	289.5	407.2
300 ppm NTP	717.6	536.2	537.4	197.7	205.4	139.1 130.6	290.4	405.7
3 ppm NTA	717.9	536.1	537.4	196.5	204.4	—	289.7	405.5
300 ppm NTA	717.1	536.1	537.2	196.5	205.3	—	290.3	405.9

FIGURE 3: XPS spectra of Cl<sub>2p</sub> (1) in sea water, (2) in presence of 300 ppm of NTP and (3) in presence of 300 ppm of NTA.FIGURE 5: XPS spectra of N<sub>1s</sub> (1) in presence of 300 ppm of NTP and (2) in presence of 300 ppm of NTA.FIGURE 4: XPS spectra of P<sub>2p</sub> in presence of 300 ppm of NTP.

indicates the presence of FeO and FeOOH [17]. A peak at 205.4 eV of Cl<sub>2p</sub> indicates adsorbed Cl<sup>-</sup> over the metal surface. The other peak at 197.7 eV indicates formation of complex [Fe-OH-Cl-NTP]<sub>ad</sub> with the inhibitor molecule on the metal surface. These peaks for Cl<sub>2p</sub> spectrum indicate certain amount of Cl<sup>-</sup> inclusion in the passive film consisting of iron oxide hydroxide. The amount of O and Cl<sup>-</sup> present over mild steel indicated that after a first stage of adsorption, an

oxide-hydroxide-chloride layer is formed. Rossi et al. [4] have suggested that chloride ions are repelled by PO<sub>3</sub><sup>3-</sup> away from the metal surface. This decreased the adsorption of chlorides leading to higher resistance against localized corrosion. Phosphorus showed two P<sub>2p</sub> peaks at 139.1 eV and 130.6 eV. The P<sub>2p</sub> peak at 139.1 eV is shifted from the characteristic elemental binding energy of 130.0 eV for P 2p<sub>3/2</sub> and 131.0 eV for P 2p<sub>1/2</sub> [18]. It can be attributed to presence of phosphorus from NTP in the surface film over the metal surface leading to uniform coverage. The other peak at 130.1 eV is due to formation of metal phosphorus adduct over the mild steel. The change in binding energy implies decrease in electron cloud over P-O and shift towards iron surface. One peak for N 1s is observed at 405.7 eV, which is shifted from

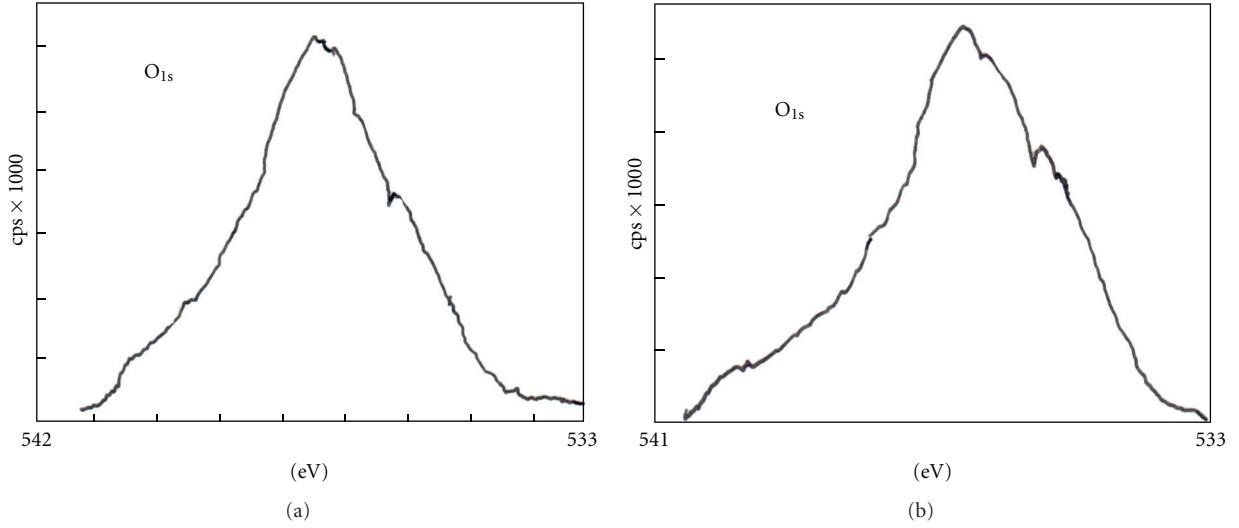


FIGURE 6: XPS spectra of O<sub>1s</sub> (a) in presence of 300 ppm of NTP and (b) in presence of 300 ppm of NTA.

characteristic value of 398.0 eV [18]. This shift may be attributed to presence of NTP molecule in the surface film in the form of a complex with the metal [19]. For 3 ppm of NTP, more amount of iron is found as compared to 300 ppm. Two peaks for Cl are observed with increasing amount at 203.7 eV while that at 197.6 eV almost remains the same as compared to 300 ppm NTP suggesting complex formation with the inhibitor over the surface. Only one peak for P<sub>2p</sub> is observed at 140 eV indicating presence of NTP on the metal surface. The amount of phosphorus is less than that obtained for 300 ppm NTP suggesting lesser adsorption.

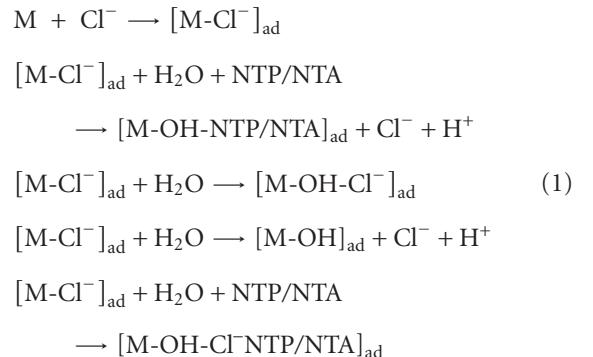
In case of 300 ppm NTA, the amount of iron found on the surface is quite high as compared to NTP (Figure 2(3)). There is little shift in binding energy of iron and oxygen indicating less compound formation. Two peaks of Cl<sup>-</sup> indicate formation of complex as well as adsorption over metal surface. The amount of Cl<sup>-</sup> at 196.5 eV is less and that at 205.3 eV is more than those obtained for NTP (Figure 3(3)). Only one peak for N<sub>1s</sub> is found at 405.9 eV, and the amount is less than that obtained for NTP indicating lesser adsorption of the inhibitor (Figure 5). Two peaks for O<sub>1s</sub> indicate the presence of both oxide and hydroxide of iron (Figure 6(b)). The presence of these elements suggests complex formation with the metal on the surface. The amounts of iron and chloride are higher, and those of C, N, O, Cl (196.5 eV) are lower in case of 3 ppm NTA as compared to 300 ppm NTA suggesting very small surface coverage. The amount of iron present in this case can be compared to that for sea water.

These observations show decrease of electron cloud density of the P-O bond due to shift of electron cloud density from O to Fe atom in case of phosphonic acid molecules [20]. These studies also reveal that NTP molecules are strongly adsorbed over mild steel surface even in presence of chloride ions. These observations confirm the formation of [Fe-OH-NTP]<sub>ad</sub> and [Fe-OH-Cl-NTP]<sub>ad</sub> film over mild steel surface in case of NTP and [Fe-OH-Cl-NTA] film over the mild steel surface in case of NTA. The formation of Fe-NTP complex is

a kind of ternary surface complex composed of metal ions, NTP, and solid precipitates of ferric hydroxide or ferric oxide on the surface of mild steel. This makes the film compact, steady, and complete, which resists mass transport and retards permeation of corrosion products through the film. The lower inhibition efficiency in case of NTA can be attributed to noncompactness of the [Fe-OH-Cl-NTA]<sub>ad</sub>, [Fe-OH-NTA]<sub>ad</sub> layers formed over the mild steel surface.

**3.3. Scanning Electron Micrographs.** The surface micrographs of mild steel treated with sea water with and without inhibitors are shown in Figure 7. It can be seen from Figure 7(a) that severe corrosion takes place in case of mild steel treated with sea water only and there is formation of corrosion products on the surface. Corrosion is less in case of mild steel treated with sea water in presence of 300 ppm of NTP (Figure 7(b)). In case of mild steel treated with sea water in presence of 300 ppm NTA, as shown in Figure 7(c), seems to be more corroded than 300 ppm of NTP but less than that with only sea water. It can be inferred that the surface film formed by inhibitors exhibits good protection for mild steel.

The following mechanism can be proposed for inhibition of corrosion of mild steel in chloride medium in presence of these inhibitors:



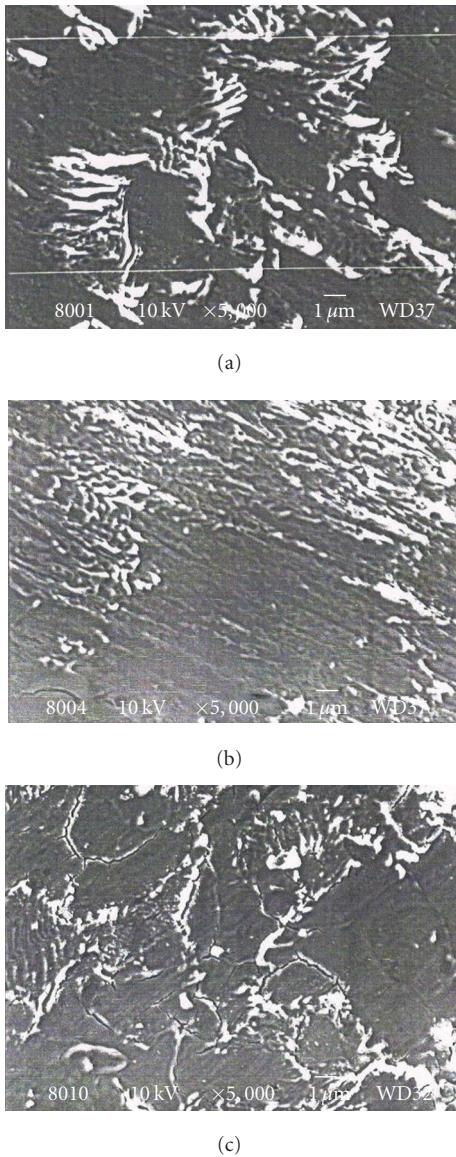


FIGURE 7: SEM of mild steel in (a) sea water, (b) sea water in the presence of 300 ppm of NTP, and (c) sea water in the presence of 300 ppm of NTA.

#### 4. Conclusions

- (i) Both NTP and NTA inhibit corrosion of mild steel in sea water, although the NTP performs better than NTA.
- (ii) Inhibition efficiency increases with increase in concentration of NTP till 100 ppm, and then it decreases whereas the inhibition efficiency increases with increase in concentration of NTA.
- (iii) NTP is a mixed type of inhibitor whereas NTA is cathodic type of inhibitor.
- (iv) NTP shows higher inhibition efficiency against corrosion of mild steel in sea water than NTA because

it forms stable  $[Fe-OH-NTP]_{ad}$  and  $[Fe-OH-Cl-NTP]_{ad}$  complexes over the metal surfaces.

- (v) The results of SEM are in correlation with the results of electrochemical and ESCA studies.

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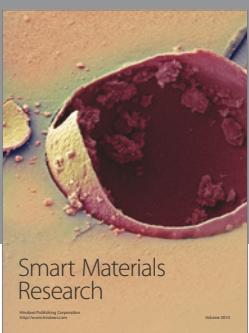
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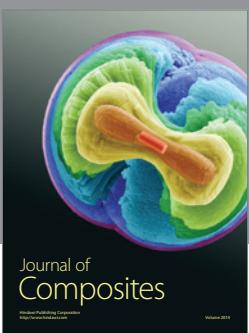
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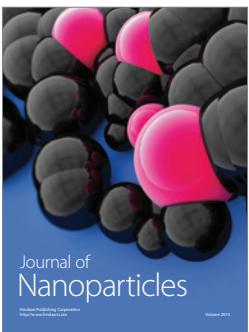


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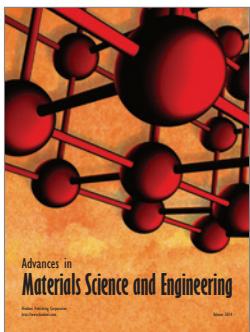
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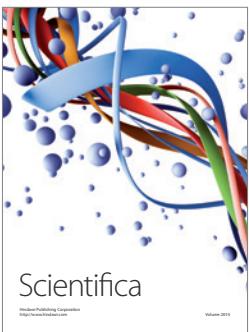
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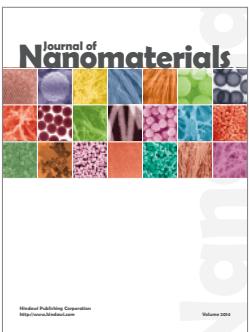
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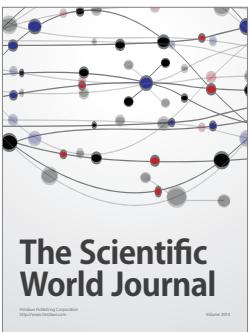
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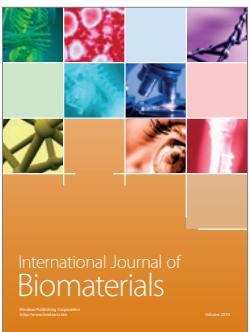
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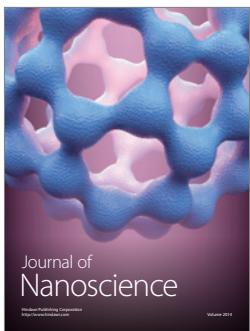
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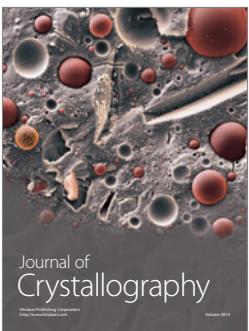
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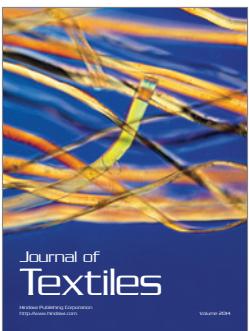
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